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INVESTIGATION OF LUMINOL AND COLLECTION
TAPE COMPONENTS AND THE EFFECTS OF AIR-
BORNE INTERFERENTS ON THE XM19 DETECTOR

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Second Quarterly Progress Report

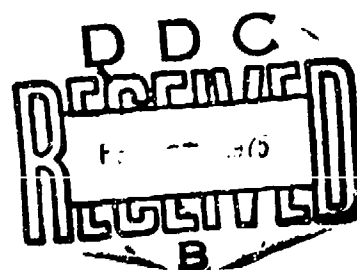
to

Development and Engineering Directorate
EDGEWOOD ARSENAL
Aberdeen Proving Ground, Maryland 21010

by

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ABSTRACT

Additional studies on the stability of solid oxidants showed that sodium perborate monohydrate ($\text{NaBO}_3 \cdot \text{H}_2\text{O}$) can be satisfactorily stored in a sealed packet if adsorbed water or water present as the tetrahydrate is removed by vacuum drying at a slightly elevated temperature and if the packet is made of a water-impermeable material. Neither sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) nor sodium pyrophosphate peroxyhydrate ($\text{Na}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$) can be successfully stored at 65°C . Further studies of the use of premixed luminol-peroxide solutions in the "Chemi II" breadboard instead of separate solutions showed the advantages of the premix solution with respect to reagent noise levels and the effect of aging of the solutions. In preliminary studies of interference by dusts, suspensions of Fort Carson dust, Edgewood dust, and a dust sample obtained on the Institute premises, all at a concentration of 0.4 mg/ml, gave responses in the "Chemi II" breadboard equivalent to that of SM cells at 1×10^5 cells/ml. Qualitative results indicated that nitric oxide and nitrogen dioxide are not likely to cause interference at atmospheric concentration levels.

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INVESTIGATION OF LUMINOL AND COLLECTION TAPE COMPONENTS
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I. INTRODUCTION

This contract is concerned with a study of several aspects of the development of the XM19 biological aerosol detector. The detection principle is based on the iron porphyrin-catalyzed oxidation of luminol in alkaline solution by hydrogen peroxide, the result of which is the chemiluminescent emission of light. Sampling of biological materials in air is accomplished with a "collector-concentrator", which isolates and concentrates particles in the respirable size range, and a continuously moving collection tape, which collects these particles by impaction. The biological particles are removed from the tape by washing it continuously with water. The wash water is mixed with the chemical reagents and the intensity of the emitted light is measured with a photomultiplier tube. The photomultiplier views the reaction mixture at two different intervals of time after the reagents are mixed with the sample. Measurement of the ratio of the two signals permits discrimination against some interferents, depending on differences in reaction rates.

Of primary concern in this investigation are the effects of airborne interferents, the development of collection tape components, and further study of the luminol chemical system for the XM19 detector.

Previous research related to the subject of this contract was performed under a subcontract with The Bendix Corporation (Prime Contract No. DAAA15-73-C-0011) during the period from November 1972 to April 1974. In the period represented by the First Quarterly Report of the current contract, several topics related to the collection tape and the chemistry of the detection system were studied.

During the period covered by this Second Quarterly Report, studies were conducted concerning the storage of solid oxidants and the use of a luminol-perborate premix; also, investigations of the problems caused by dust interferences were begun.

II. STORAGE STABILITY OF SOLID OXIDANTS

In the period covered by the First Quarterly Report, work on this topic was intensified. In this second quarter, however, the experiments concerning the storage of solid oxidants at elevated temperatures were essentially concluded. The remaining effort is to be an evaluation of analytical methods for determination of the water content of sodium perborate monohydrate ($\text{NaBO}_3 \cdot \text{H}_2\text{O}$) for possible use in a procurement specification.

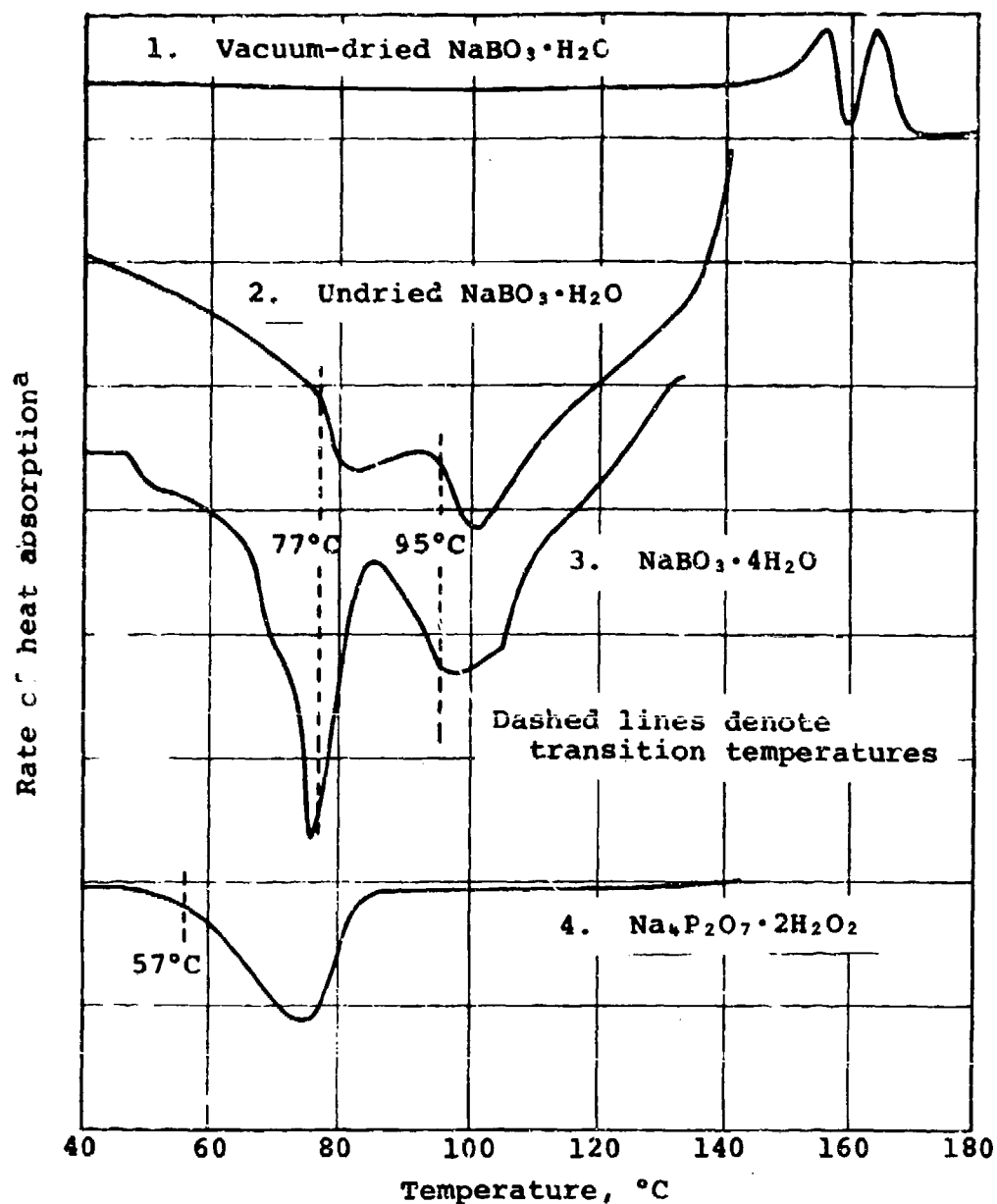
A. Differential Scanning Calorimetry of Solid Oxidants

Because of the storage problems experienced by Bendix with sodium perborate monohydrate ($\text{NaBO}_3 \cdot \text{H}_2\text{O}$) at elevated temperatures, some effort was expended in studying the thermal stability of $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ and an alternative solid source of hydrogen peroxide, sodium pyrophosphate peroxide ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$). Using differential scanning calorimetry (DSC), it was found that an undried sample of $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ underwent two irreversible endothermic transitions, one at 77°C and the other at 95°C . Below 77°C , the undried $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ appeared thermally stable. However, in the case of the undried $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$, a single irreversible endothermic transition occurred at about 57°C , indicating thermal instability at a storage temperature of 65°C . These DSC curves are illustrated in the figure on page 3.

On the basis of these preliminary DSC data the $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ appeared to be the more thermally stable source of hydrogen peroxide.

In additional experiments, samples of $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ that were dried at 65°C and at a reduced pressure of 0.05 mmHg for a 12-hr period were thermally analyzed on the differential scanning calorimeter. Also, samples of sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) were subjected to identical analyses. The $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ samples showed the same thermal transitions at 77 and 95°C that were observed for the undried $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ except that the intensity was greater for the $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ samples. On the other hand, the vacuum-dried sample of $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ showed no thermal transitions below 140°C . In fact, the samples exhibited two mildly exothermic transitions at approximately 150 and 165°C , as shown in the figure.

These results strongly suggest that the thermal transitions observed for the undried $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ (out-of-the-bottle) were, indeed, due to the presence of a $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (tetrahydrate) component in the undried monohydrate. Furthermore, the dried $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ showed an essentially negligible loss of available hydrogen peroxide upon analysis after the vacuum-drying process. Therefore, it can be concluded that the endothermic transitions at 77 and 95°C



DSC Curves for Solid Oxidants

- a. The ordinate scales and scan rates for each curve are as follows:
1. 0.6 (cal/g-sec)/div. at 10°C/min
 2. 0.017 (cal/g-sec)/div. at 5°C/min
 3. 1.08 (cal/g-sec)/div. at 10°C/min
 4. 0.04 (cal/g-sec)/div. at 5°C/min

were due to reactions involving the loss of water of hydration of the tetrahydrate form and were not due to any reaction involving the available hydrogen peroxide.

It should not be inferred from these DSC data, however, that the vacuum-dried $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ would be stable in storage at temperatures up to 140°C . The loss of hydrogen peroxide would be greatly accelerated at these higher temperatures regardless of the nature of the sample pretreatment. The DSC data simply indicate that the tetrahydrate-to-monohydrate transition occurs at temperatures lower than transitions involving the available hydrogen peroxide of the dried $\text{NaBO}_3 \cdot \text{H}_2\text{O}$.

Also, it is evident that DSC measurements of this type could serve as a sensitive indicator of the undesirable presence of the tetrahydrate form of sodium perborate contained in the monohydrate form. In earlier investigations it was established that the tetrahydrate form cannot be successfully stored at elevated temperatures sealed in a blister packet. When contained in a sealed packet, the tetrahydrate quickly loses water vapor at elevated temperatures, which, in turn, causes the decomposition of the peroxy linkages of the perborate with the loss of hydrogen peroxide. The hydrogen peroxide then decomposes to additional water (vapor) and oxygen, which quickly builds an excessive internal pressure in the sealed packet. Thus, the presence of any tetrahydrate in the monohydrate becomes undesirable relative to the stability of the solid oxidant upon storage at elevated temperatures in a closed system.

B. Storage of Solid Oxidants

The final effort in the study of the storage stability of sodium perborate monohydrate ($\text{NaBO}_3 \cdot \text{H}_2\text{O}$) and sodium pyrophosphate peroxide ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$) was to evaluate several sealed packages of each compound after extended storage at 60°C . In order to obtain results that would be statistically meaningful, ten 1-g packages of each oxidant— $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$ —were prepared using Scotchpak 45AX48 heat-sealable Mylar to form a tightly sealed blister packet. The packets were then stored at 60°C and 80 to 90% relative humidity for a period of 2 weeks. After the storage period, the packets appeared unchanged, i.e., none of the packets were ruptured because of excessive internal pressure and all of the powders remained free-flowing. At this point the powders were removed from the packets and assayed for their available hydrogen peroxide content by titration with standard potassium permanganate solution. The ten $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ packets were found to contain after storage an average of 31.93% H_2O_2 with a relative standard deviation of 0.26%. This value compared with an available H_2O_2 content of 32.40% for the $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ before storage. The ten $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$ packets were found to contain an average of 17.88%

H_2O_2 after storage with a relative standard deviation of 0.27%. The $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$ contained 18.21% H_2O_2 before storage. These results demonstrated a relative loss upon storage of 1.45% and 1.81% in H_2O_2 content for $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$, respectively. These losses would probably have been smaller if the packets had been sealed with a material that was less permeable to water vapor than Mylar.

Thus, it appears from these results and other results presented in earlier reports, that $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ can be safely stored at elevated temperatures ($\sim 60^\circ\text{C}$) with the exclusion of water vapor. However, the 45AX48 Mylar does not appear to provide an adequate barrier to water vapor. In addition, contact of the $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ blister packet with the 0.1% EDTA solution, over which the blister packet is to be stored in the field kit, was found to increase the water permeability of the Mylar because of the alkalinity of the solution. In fact, in the presence of a stronger alkali, 0.1 M NaOH solution, the 45AX48 Mylar was found to be even more permeable to water than in the presence of the EDTA solution. This was evidenced by the rapid build-up of pressure and subsequent rupture of the packet.

It was also established in this series of experiments that the $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ powder could be successfully vacuum-dried at temperatures up to 75°C with no appreciable loss of H_2O_2 . Indeed, the H_2O_2 content was found to increase slightly over a period of 12 hr because of the loss of water from the tetrahydrate impurity and adsorbed water from the $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ crystals under conditions of vacuum and elevated temperature.

In conclusion, it appears that vacuum drying of the $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ powder at elevated temperatures is probably the best way to prepare the dry powder for sealing in a closed packet. This process insures the removal of any adsorbed water that could otherwise cause decomposition of the $\text{NaBO}_3 \cdot \text{H}_2\text{O}$.

III. PREMIX EVALUATIONS

This topic was addressed in some detail in the First Quarterly Report on this contract. In this quarter, only a limited amount of additional work with the premix was conducted on the "Chemi II" breadboard apparatus. This restriction on additional premix experimentation was exercised in anticipation of the receipt of an XM19 detector. It was assumed that with the XM19 Phase III detector, the premix evaluations would take on additional significance. The XM19 detector (Serial Number 12) was subsequently received near the end of this quarter of investigation. Thus, the limited amount of premix work completed in this

quarter on the "Chemi II" breadboard will be covered in this report. The more relevant premix evaluations in the XM19 hardware will be related in future reports.

Because of the successful experiments conducted in the past with a luminol-perborate premix, it was of interest to compare the breadboard responses obtained with separate luminol and perborate solutions to those obtained with the premix solution. The comparison was made in terms of response magnitudes and reagent background noise. The separate luminol solution contained 8 mg/ml of NaOH, 3 mg/ml of EDTA (tetrasodium salt), and 0.2 mg/ml of luminol; the separate perborate solution contained 1% $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ and 0.1% EDTA; and the premix solution contained 4.8 mg/ml of NaOH, 4.0 mg/ml of EDTA, 2.5 mg/ml of $\text{NaBO}_3 \cdot \text{H}_2\text{O}$, and 0.2 mg/ml of luminol. The responses were recorded for an SM suspension challenge of 1×10^5 cells/ml in the "Chemi II" hardware. The challenge suspension was added at a mixing "tee" just prior to a 1-sec exposure to the photomultiplier tube in a clear tubing reaction cell. The table on page 7 shows the results of the comparisons for two luminol samples. All solutions were used after being freshly mixed except where noted.

In nearly all cases, the comparison of the premix to the separate solutions was favorable. The SM responses were essentially the same with either system. The advantages of the premix included reagent noise levels of reduced magnitude and less solution aging effect. The difference in solution aging is contrasted by the data in the table. For a particular sample of Baker 1-8018(1) luminol, which invariably gives high initial reagent backgrounds due to some unknown contamination, the separate solutions yielded a reagent background that was an order of magnitude larger than the premix with the same luminol. The SM responses for the separate solutions were not detectable in the presence of the larger reagent background; the usual responses for the premix were observed. After these solutions had aged for a period of approximately 5 hr, the reagent background of the separate solutions had dropped to approximately half the initial value and the SM response was then detectable over the background. However, the reagent background and SM responses of the premix solution changed only slightly during the aging period.

These results again demonstrated the utility of the premix for the initial stabilization of the reagents. Because the possibility of solution contamination is greater for field use of the XM19, the ability of a premixed solution to insure reproducible performance--both initially and long-term--seems to be a desirable characteristic for the XM19 chemical system.

Comparison of Separate Luminol-Perborate Solutions
to a Premixed Solution

Luminol	Reagent background, mV	Net SM response, mV
<u>Baker Lot 214002</u>		
Separate solutions	105 ± 15	165 ± 25
Premixed solution	95 ± 5	170 ± 10
<u>Baker Lot 1-8018(2)^a</u>		
Separate solutions	55 ± 5	85 ± 10
Premixed solution	50 ± 5	85 ± 5
<u>Baker Lot 1-8018(1)^b</u>		
Separate solutions	630 ± 100 (245 ± 25) ^c	0 ^d (245 ± 35) ^c
Premixed solution	45 ± 5 (55 ± 5) ^c	150 ± 10 (220 ± 15) ^c

- This lot of Baker 1-8018 was obtained from Edgewood Arsenal in December 1973.
- This lot of Baker 1-8018 was obtained from Bendix in November 1972.
- The values in parentheses are for solutions aged 5 hr after mixing.
- The net response to SM was negligible (zero) in the presence of the large background.

IV. INTERFERENCE STUDIES

Because interference studies also take on added significance when the evaluations are conducted with the XM19 hardware rather than the "Chemi II" breadboard, experiments of only limited scope with interferents were performed in this quarter. Again, reports of investigations of dust interferences in the XM19 hardware will be deferred until a later date. In this quarter, a preliminary investigation of the dust problem was made with the use of the "Chemi II" hardware; the effects of large concentrations of the gases NO and NO₂ on the SM responses in the "Chemi II" hardware were also evaluated.

A. Dust Interferences

Because of problems caused by dust interferences in the XM19 detector, a study was made of dust samples from several sources and the influence of these dusts on the luminol- H_2O_2 reaction in the "Chemi II" hardware. Samples obtained from Edgewood Arsenal labeled "Fort Carson dust" and "Edgewood dust" in addition to a sample obtained from the Institute premises were compared for their chemiluminescence responses. All samples were screened and aqueous suspensions of the portions passing a 200-mesh screen were used as challenges. It was found that a suspension concentration of approximately 0.4 mg/ml was necessary to give a breadboard response equal in magnitude to the response obtained with an SM challenge of 1×10^5 cells/ml. Also, no significant differences in breadboard responses were found for the three dust samples.

In addition, when a suspension of "Edgewood dust" was filtered through Whatman No. 541 paper, the filtrate gave no detectable response. This result indicated that the insoluble material (possibly microorganisms) was responsible for the chemiluminescence reaction.

B. Interference by the Atmospheric Contaminants NO and NO₂

As an initial effort in the preliminary investigation of potential gaseous interferents, two common atmospheric contaminants—NO and NO₂—were tested for interference in SM detection with the "Chemi II" hardware. The concentrations of these gases that were used in the initial investigation were 2000 ppm of NO and 100 ppm of NO₂. Because these gas concentrations are orders of magnitude larger than any that would be expected in the field, the results were essentially qualitative in nature.

When 100 ppm of NO₂ or 2000 ppm of NO was added to the dilution air in the SM aerosol generator, the effects on the background and net SM response were noted. No interference by NO₂ could be detected at the 100 ppm level. That is, the background was unaffected and the SM response was essentially unchanged with or without the addition of NO₂. However, in the presence of 2000 ppm of NO, the SM response was suppressed to one-half the magnitude of the response obtained in the presence of no added NO. The background (no SM challenge) was unaffected by the 2000 ppm of NO.

Although interference by NO was noted in this investigation, it is quite likely that no bio-detection interference could be ascribed to gaseous NO at levels at which it exists in an urban atmosphere. The mechanism of the SM suppression by gaseous NO is unknown at this time.

V. FUTURE PLANS

With the receipt of an XM19 detector, the studies concerning the dust interference problem will be intensified during the next quarter. Also the evaluation of a luminol-perborate premix will be initiated in the XM19 hardware.

Investigations concerning an analytical method for estimation of the water content of $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ will also be conducted in the next quarter. This method should serve as a quality control criterion in a procurement specification for $\text{NaBO}_3 \cdot \text{H}_2\text{O}$.

Additionally, in the next quarter, a feasibility study on the electrolytic production of H_2O_2 in the XM19 will be reported.

VI. ACKNOWLEDGMENTS

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